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Mon-linear optical material and non-linear optical device employing it.

A novel organic non-linear optical material and a device using the same are disclosed. The material hardly makes reversal symmetrical molecular configuration in a bulk state such as a crystal and a thin layer and shows a high non-linear optical effect. A non-linear optical device using the material has an excellent properties. The organic non-linear optical material is comprised of the following compound:

$$R_{i} \leftarrow \bigvee_{\substack{N \\ R_{i}}}^{R_{i}}$$

wherein R₁, R₂ and R₄ are independently a hydrogen atom, a cyano group, a phenyl group, an amino group, an alkoxy group, an acytamino group, an alkylthio group, an alkyl group, an alkoxyycarbonyl group, carbamoyl group or a heterocyclic group, provided that Rs is allowed to link together with Rs to form a ring and R1. R3 and R4 are not hydrogen atom at the same time; R2 is a hydrogen atom, an alkyl group or an acyl group; and said groups represented by R1. R2, R4, R4 and the ring formed by linking the groups represented by R₂ and R₄ are allowed to have a substituent.

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NON-LINEAR OPTICAL MATERIAL AND NON-LINEAR OPTICAL DEVICE EMPLOYING IT

FIELD OF THE INVENTION

This invention relates to an organic non-linear optical material applicable to the generation of the higher harmonic waves and to the parametric amplification of laser beam, and to the like, and further relates to an organic non-linear optical device, employing it.

BACKGROUND OF THE INVENTION

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A non-linear optical effect is strikingly displayed when exposing a material to intensive light such as laser beams. Such effect can be applied to a frequency conversion, an intensity moduration, a switching operation, and so forth. In recent years, many reassarches and developments have been made for obtaining the materials capable of displaying such a non-linear optical effect so far, Regarding such research and development of the non-linear optical material, "Non-linear Optical Properties of Organic Molecules and Crystals, vol. 1, 2, edited by AT & T, Academic Press Inc. "87", can be referred.

For the frequency conversion and, in particular, for the Second Harmonic Generation (hereinafter abbreviated to SHG) originated from the second-order non-linear optical effect, there have been some indications of the possibility that an organic compound may display extraordinarily higher efficiency than those of the conventionally known inorganic materials such as lithium niobate (LiNbO₃), potassium dihydrogenphosphate (KDP), and so torth. Such an indication is found out in, for example, "Organic Non-linear Optical Materials", complied under the supervision of Masao Kato and Hachiro Nakanishi, published by C.M.C. Company, Japan, 1985,

The optical non-linearity of an organic compound originates from π electrons of molecules, and the second-order non-linear molecular polarizability (β) becomes particularly greater when the above-mentioned compound has both of an electron donative group and an electron attractive group.

There are, however, many compounds including, typically, p-nitroaniline which display no SHG at all or a few in their crystalline arrangement, even if they have a great molecular non-linear polarizability. This is because the molecular orientation in the crystals of polar organic compounds are liable to be centrosymmetric in crystalline arrangement.

SUMMARY OF THE INVENTION

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It is, accordingly, an object of the invention to provide a novel organic non-linear optical material which can hardly be inversely symmetric in a bulk state such as those of crystals, thin films and so forth and is capable of displaying a high non-linear optical effect and, further, an organic non-linear optical device employing the material.

The above-mentioned object of the invention can be achieved with a non-linear optical material comprised of a compound represented by the following Formula I and a non-linear optical device employed the above-mentioned material.

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Formula I

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$$R_1 \stackrel{N}{\underset{R_2}{\bigvee}} R_4$$

wherein R1. R2 and R4 independently a hydrogen atom, a cyano group, a phenyl group, an amino group, an

alkoxy group, acytamino group, an alkytithio group, an alkyt group, an alkoxycarbonyl group, a carbamoyl group, or a heterocyclic group, provided that R₂ is allowed to link together with R₄ to form a ring and R₁. R₂ and R₄ shall not be hydrogen atoms at the same time; R₂ is a hydrogen atom, an alkyl group or an acyl group, and the groups represented by R₁. R₂, R₄ and the ring formed by linking the groups represented by R₂ and R₄ are allowed to have a substituent.

DETAILED DESCRIPTION OF THE INVENTION

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The invention will now be more detailed below.

In the above-given Formula I, amino groups represented by R_1 , R_2 and R_4 include, for example, a methylamino group, a dimethylamino group and so forth.

Alkoxy groups represented by R₁, R₂ and R₄ include, for example, a methoxy group, an ethoxy group, and so forth

Acytamino groups represented by R_1 , R_2 and R_4 include, for example, a benzamido group, an acetoamido group, and so forth.

Alkytthio groups represented by R₁, R₂ and R₄ include, for example, a methythio group, and so torth.

Alkyt groups represented by R₁, R₂ and R₄ include, for example, a methyl group, an ethyl group, and

20 so forth.
Alkoxycarbonyl groups represented by R₁, R₂ and R₄ include, for example, a methyl carboxylate group, and so forth.

Carbamoyl groups represented by R_1 , R_3 and R_4 include, for example, a methylcarbamoyl group, a phenylcarbamoyl group, and so forth.

Heterocyclic groups represented by R₁, R₂ and R₄ included for example, a pyridyl group, a pyrazolyl group, an imidazolyl group, a pyrimidyl group, a turyl group, a thienyl group, and so forth.

The preferable groups represented by R_1 , R_2 and R_4 include, for example, a substituted phenyl group. The preferable rings completed by linking R_3 and R_4 together include, for example, a benzene ring.

The rings completed by linking R₂ and R₄ together are allowed to have a substituent.

Alkyl groups represented by R₂ include, for example, a methyl group, an ethyl group, and so forth.

Acyl groups represented by R₂ include, for example, a benzoyl group, an acetyl group, and so forth.

The preferable ones represented by R₂ include, for example, a hydrogen atom.

Rt. Rs. Rs and Rs are each allowed to have a substituent.

There is no special limitation to the substituents, but they may be selected from the following electron attractive or electron donative substituents.

The above-mentioned electron attractive substituents are those having a Hammett's constant op more than zero. They include, for example, nitro groups, cyano groups, alkylsulfonyl groups such as a methylsulfonyl group, a ethylsulfonyl group and so forth, formyl groups, carbamoyl groups such as a methylsulfonyl group, a phenylcarbamoyl group, and so forth, sulfamoyl groups such as a methylsulfamoyl group, and so forth, oxycarbonyl groups, and so forth, group, and so forth, dicyanovinyl groups, carboxy groups, and so forth.

Among these, a nitro group, a cyano group, an alkylsulfonyl group, a formyl group and an alkoxycarbonyl group are preferable.

The above-mentioned electron donative substituents are a halogen atom or those having a Hammett's constant σ_P less than zero. They include, for example, amino groups such as an amino group, a methylamino group, a dimethylamino group, a L-2-hydroxymethyl-1-pymoldinyl group, and so forth, hydroxyl groups, alkoxy groups such as a methoxy group, an ethoxy group, a butoxy group, and so forth, alkyl groups such as a methyl group, an ethyl group, a propyl group, and so forth.

The compounds represented by Formula I preferably include, for example, those having R₁ representso ing a phenyl group substituted with an electron attractive substituent and R₄ representing a phenyl group
substituted with an electron donative substituent, or those having R₁ representing a phenyl group
substituted with an electron donative substituent and R₄ representing a phenyl group substituted with an
electron attractive substituent.

The compounds preferably applicable to the invention will be exemplified below. It is, however, to be understood that the invention shall not be limited thereto.

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The imidazole rings of the compounds relating to the invention may usually be synthesized by making use of amidine having R₁ and bromacetophenone having R₂ and R₄. For further details, refer to Chemische Berichte, 34, 637 and, idem, 29, 2097, for example.

The other known synthesizing methods are described in, for example, Chemische Berichte 38, 1531. id. 35, 2630, Annalen der Chemie, 600, 95-108, id. 663, Synthesis, 1978, 6, Journal of Chemical Society, 1957, 4225, and so forth.

The benzimidazole rings of the compounds relating to the invention are usually synthesized through a dehydration reaction of an o-phenylenediamine derivative with a carboxylic acid derivative.

When R₂ represents an alkyl group or an acyl group, the Imidazole rings may be synthesized by reacting imidazole with the corresponding alkyl halide or an acid chloride in the presence of base, or they may also readily be synthesized by selecting the raw materials for completing a ring.

Synthesis Example 1

Synthesis of Exemplified Compound 1

A solution was prepared by dissolving 15 g of 4-aminosalicytic acid and 11 g of phenylenediamine in 150 m1 of dioxane, and 20 g of N,N'-dicyclohexylcarbodiimide was dropped into the solution so as to react them for 4 hours at room temperature. Urea and, then, the solvent were removed from the solution. The resulting solution was heated for 1 hour at 120°C and, then, refined. Yield was 10 g. The total amount thereof was dissolved in 100 ml of acetonitrile and 7 g of benzoyl chloride was added. The resulting solution was refluxed for 3 hours, and the resulting reacted solution was cooled down, so that 13 g of the objective crystals were obtained. The structure of the crystals were confirmed with an NMR and an FD mass-spectrometer.

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Synthesis Example 2

Synthesis of Exemplified Compound 6

p-nitrobenzamidine of 10.25 g was suspended in 50 ml of dimethyl formamide and 3.11 g of bromacetophenone was then added to the suspension. The suspension became exothermic and the color thereof was changed into reddish-brown. After the reddish-brown solution was cooled down, water was added. The resulting solid matters deposited were filtrated.

Yield: 2.27 g

The structure of the solid matters were confirmed with an NMR and an FD mass-spectrometer.

Melting point: 231°C

Synthesis Example 3

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Synthesis of Exemplified Compound 7

o-aminoacetophenone of 6.75 g was dissolved in 60 ml of acetonitrile. Pyridine of 5 ml was added. Benzoyl chloride of benzoyl chloride was dropped in while stirring. After 3 hours, the solvents were distilled off under reduced pressure. An extraction was carried out by adding water and ethyl acetate. An organic layer was dehydrated with anhydrous magnesium sulfate and then the solvents were distilled off.

A crystallization deposition was carried out with alcohol. White crystals of o-benzamidobromacetophenone were thereby obtained. Yield: 9.6 g

In place of the bromacetophenone used in Example 2, 4.97 g of o-benzamidobromacetophenone prepared as mentioned above was so used as to be reacted in the same manner as in Example 2, and a recrystallization was carried out with alcohol. Yield: $3.65 \, g$

The structure of the resulting matter was confirmed with an NMR and a FD mass-spectrometer.

Meting point: Not lower than 250 °C

The compounds of the invention may be used as a non-linear optical device, when the compounds are in various forms including, for example, a single-crystalline form, a powder form, a liquid form, thin films such as Langmuir-Blodgett film, a vacuum-evaporated film and so forth, the other forms in which the compound is blended in polymers or liquid-crystal molecules, and so forth. The compounds of the invention may also be made pendent to a polymer or used as a clathrate compound or an addition product.

When a non-linear optical device is applied to the non-linear optical material of the invention, such device may be in any publicly known waveguide form. As is described in Japanese Patent O.P.I. Publication No. 63-77035/1988, these forms include, for example, a fibre form, a tabular form, and a form in which a single crystal is surrounded by a cladding material.

The non-linear optical devices of the invention may be frequency conversion and modulation of laser beams, i.e., generation of the higher harmonic wave, parametric amplification, intensity modulation, optical switching, and so forth.

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EXAMPLES

Now, the examples will be described below, it is, however, to be understood that the embodiments of the invention shall not be limited thereto.

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Example-1

The compounds of the invention were evaluated for judging the SHG effect, by the well-known powder method. (Refer to S.K. Kurtz and T.T. Perry; J. Appl. Phys., 39, 3798, 1968)

The following light source was used. A Q-switched NdtYAG laser (the wavelength is 1084 nm) Model YG680A manufactured by Quantel International, Inc., U.S.A., having a beam diameter of 2 mm, a repetition rate of 10 pps, a pulse width of 10 ns, and a pulse energy of 20 mJ. A powdered sample filled in a glass-cell was exposed to the laser beam. The produced SHG light, 532-nm green light, was spectrally separated by means of a filter and a monochrometer, and intensity of which was detected by means of a photomultiplier tube, so as to obtain the intensity of SHG of each sample relative to that of urea which is regarded as a value of 1.

The results thereof are also shown in Table 1, below.

Table 1

Compound	SHG Intensity	Remark Comparative	
Urea	1 for Standard		
m-nitroaniline	8	Comparative	
Example 1	7	Invention	
Example 4	10	Invention	
Example 8	15	Invention	
Example 7	18	Invention	
Example 15	8	Invention	

As is apparent from Table i, it can be found that the compounds of the invention are excellent non-linear optical materials high in SHG intensity.

Example 2

The same compounds of the invention as those used in Example 1 were crystalized inside a hollow glass fibre so as to make the non-linear optical devices. When the Nd:YAG laser beam was coupled into these devices from the end-face of the fibre.

Claims

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1. A non-linear optical material comprised of a compound represented by the following Formula I:

$$R_1 = \begin{pmatrix} N & R_4 \\ N & R_3 \end{pmatrix}$$
 (I)

wherein R₁, R₂ and R₄ are independently a hydrogen atom, a cyano group, a phenyl group, an amino group, an alkoxy group, an acylamino group, an alkylthio group, an alkyl group, an alkoxycarbonyl group, a carbamoyl group or a heterocyclic group, provided that R₂ is allowed to link together with R₄ to form a ring and R₁, R₂ and R₄ shall not be hydrogen atoms at the same time; R₂ is a hydrogen atom, an alkyl group or an acyl group; and said groups represented by R₁, R₂, R₃, R₄ and the ring formed by linking the groups represented by R₃ and R₄ are allowed to have a substituent.

The material of claim 1, wherein said substituent is an electron attractive group selected from a nitro group, a cyano group, an alkyl sulfonyl group, a formyl group, a carbamoyl group, a sulfamoyl group, an oxycarbonyl group, dicyanovinyl group and a carboxy group.

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- 3. The material of claim 2, wherein said electron attractive group is a nitro group, a cyano group, an atkytsulfonyl group, a formyl group or an atkoxycarbonyl group.
- 4. The material of claim 1, wherein said substituent is an electron donative group selected from a hatogen atom, an amino group, a hydroxy group, an aikoxy group and an alkyl group.
- 5. The material of claim 1, wherein one of groups represented by said R₁ and R₄ is a phenyl group substituted by an electron attractive group and the other one of these groups is a phenyl group substituted by an electron donative group.
- The material of claim 1, wherein one of groups represented by R₁, R₂ and R₄ is a substituted phenyl group.
- 7. The material of claim 6, wherein a substituent of said substituted phenyl group is a nitro group, a cyano group, an alkyl sulfornyl group, a formyl group, a carbamoyl group, a sulfamoyl group, an oxycarbonyl group, dicyanovinyl group or a carbony group.
- 8. The material of claim 6, wherein a substituent of said substituted phenyl group is a halogen atom, an amino group, a hydroxy group, an alloxy group or an alkyl group.
- 9. The material of claim 1, wherein a ring tormed by linking a group represented by said R₄ and a group represented by said R₄ is a benzene ring.
 - 10. The material of claims 1 or 2 to 9, wherein said R_2 is a hydrogen atom.

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11. A non-linear optical device comprising a compound represented by the following Formula I:

$$R_1 \leftarrow N \qquad R_2 \qquad (I)$$

wherein R_1 , R_2 and R_4 are independently a hydrogen atom, a cyano group, a phenyl group, an amino group, an alkoxy group, an acytamino group, an alkylthlo group, an alkyl group, an alkoxyycarbonyl group, a carbamoyl group or a heterocyclic group, provided that R_2 is allowed to link together with R_4 to form a ring and R_1 , R_3 and R_4 shall not be hydrogen atoms at the same time; R_2 is a hydrogen atom, an alkyl group or an acyl group; and said groups represented by R_1 , R_2 , R_3 , R_4 and the ring formed by bonding the groups represented by R_3 and R_4 are allowed to have a substituent.

- 12. The device of claim 11, wherein said substituent is an electron attractive group selected from a nitro group, a cyano group, an alkyl suffonyl group, a formyl group, a carbarnoyl group, a sulfamoyl group, an oxycarbonyl group, dicyanovinyl group and a carboxy group.
- 13. The device of claim 12, wherein said electron attractive group is a nitro group, a cyano group, an alkylsulfonyl group, a formyl group or an alkoxycarbonyl group.
- 14. The device of claim 11, wherein said substituent is an electron donative group selected from a halogen atom, an amino group, a hydroxy group, an alkoxy group or an alkyl group.
 - 15. The device of claim 11, wherein one of groups represented by said R₁ and R₄ is a phenyl group substituted by an electron attractive group and the other one of these groups is a phenyl group substituted by an electron donative group.
- 16. The device of claim 11, wherein one of groups represented by R₁, R₂ and R₄ is a substituted phenyl group.
- 17. The device of claim 16, wherein a substituent of said substituted phenyl group is a nitro group, a cyano group, an alkyl suffornyl group, a formyl group, a carbamoyl group, a sulfamoyl group, an exycarbonyl group, dicyanovinyl group or a carboxy group.
- 18. The device of claim 16, wherein a substituent of said substituted phenyl group is a halogen atom, an amino group, a hydroxy group, an alkoxy group or an alkyl group.
- 19. The device of claim 11, wherein a ring formed by limiting a group represented by said R₄ and a group represented by said R₄ is a benzene ring.
 - 20. The device of claims 11 or 12 to 19, wherein said $R_{\rm 2}$ is a hydrogen atom.
 - 21. The device of claims 11 or 12 to 20, wherein said device has a waveguide form.
- 22. The cevice of claim 21, wherein said device has a fibre form.
 - 23. The device of claim 21, wherein said device has a tabular form.
- 24. The device of claim 21, wherein said device has a form in which a single crystal of said material is surrounded by a cladding material.

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ACCESSION NUMBER: DOCUMENT NUMBER:

1989:431259 CAPLUS

TITLE:

Silver halide color photographic light-sensitive

material containing novel cyan coupler from

phenylimidazole compounds

INVENTOR (S): PATENT ASSIGNEE(S):

Masukawa, Toyoaki; Nakayama, Noritaka

Konica Co., Japan

SOURCE:

Bur. Pat. Appl., 44 pp. CODEN: BPXXDW

DOCUMENT TYPE:

Patent

LANGUAGE:

FAMILY ACC. NUM. COUNT:

English 2

PATENT INFORMATION:

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BP 304856 BP 304856 R: DB, GB, IT.	A2 A3 NL	19890301 19890329	EP 1988-113668	19880823
US 5017467 PRIORITY APPLN. INFO.:	A	19910521		19901012 19870824 19880822 19900228

The title material contains a cyan coupler I [R1, R2 = substituent; R3 = AB H, alkyl, aryl, COR4, CO2R4, CONR4R5, SO2R4, SO2NR4R5 (R4 = alkyl, aryl, heterocyclic group; R5 = H, alkyl); X = H, group capable of being split off upon reaction with oxidized product of a developing agent; m = 0-4; n = 0-5]. The coupler is excellent in spectral absorption, absorption coefficient, and fastness. Thus, II was prepared and used in a color photog.

I

II

paper to produce high-d. heat-resistant dye image. 121216-54-4 121216-63-5 121216-65-7 121216-66-8

RL: TEM (Technical or engineered material use); USES (Uses) (photog. cyan coupler, for heat-resistant image)

RN 121216-54-4 CAPLUS

IT

CN Carbamic acid, [4-[2-[2-[2-[2,4-bis(1,1-dimethylpropyl)phenoxy]-1-oxohexyl]amino]phenyl]-5-chloro-1H-imidazol-4-yl]phenyl]-, ethyl ester (9CI) (CA INDEX NAME)

RN 121216-63-5 CAPLUS
CN Hexanamide, N-[2-[2-[acetylamino)phenyl]-5-chloro-1H-imidazol-4yl]phenyl]-2-[2,4-bis(1,1-dimethylpropyl)phenoxy]- (9CI) (CA INDEX NAME)

RN 121216-65-7 CAPLUS
CN Benzamide, N-[2-[4-[2-[(2-[2,4-bis(1,1-dimethylpropyl)phenoxy]-3-methyl-1-oxobutyl]amino]phenyl]-1H-imidazol-2-yl]phenyl]-2,3,4,5,6-pentafluoro-(9CI) (CA INDEX NAME)

RN 121216-66-8 CAPLUS

CN Butanamide, 2-[2,4-bis(1,1-dimethylpropyl)phenoxy]-N-[2-[5-chloro-2-[2-[3,3,3-trifluoro-1-oxopropyl)amino]phenyl]-1H-imidazol-4-yl]phenyl]-3-methyl- (9CI) (CA INDEX NAME)

IT 121216-46-4P 121216-47-5P 121216-49-7P

RL: SPN (Synthetic preparation); PREP (Preparation)

(preparation and use of, as cyan coupler for heat-resistant image)

RN 121216-46-4 CAPLUS

CN Benzenepropanamide, N-[2-[2-[2-(benzoylamino)phenyl]-5-chloro-1H-imidazol-4-yl]phenyl]-α-butyl-2,4-bis(1,1-dimethylpropyl)-β-oxo-(9CI)
(CA INDEX NAME)

RN 121216-47-5 CAPLUS
CN Carbamic acid, [2-[4-[2-[[2-[2,4-bis(1,1-dimethylpropyl)phenoxy]-1-oxohexyl]amino]phenyl]-1H-imidazol-2-yl]phenyl]-, 2-methylpropyl ester (9CI) (CA INDEX NAMB)

RN 121216-49-7 CAPLUS
CN Benzamide, N-[2-[4-[2-[[2-[2,4-bis(1,1-dimethylpropyl)phenoxy]-1-oxohexyl]amino]phenyl]-5-chloro-1H-imidazol-2-yl]phenyl]- (9CI) (CA INDEX NAME)